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DE PLANTIS TOXICARIIS E MUNDO NOVO TROPICALE COMMENTATIONES III

PHYTOCHEMICAL EXAMINATION OF SPRUCE'S ORIGINAL
COLLECTION OF BANISTERIOPSIS CAAPI

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RICHARD SPRUCE, the humble Yorkshire schoolmaster-bryologist, became one of the outstanding tropical plant explorers of all time. On July 12, 1849, he arrived at the mouth of the Amazon to start his epoch-making botanical studies and collections that spanned a period of fifteen years (1849–1864) in the Amazon and the Andes.

Spruce (Plate XXX) was far ahead of his day in scientific thought and method. He lived closely with native peoples, learned several languages and kept his mind ever inquisitive and his eye ever perceptive. For a number of plants that have later attracted extensive phytochemical and pharmacological attention — and which are still claiming serious studies — it was Spruce who gave us detailed, accurate, pioneer information.

One of these plants was a jungle liana, source of an extraordinary hallucinogenic drink called *caapi* in Brazil, *ayahuasca* in Ecuador and Peru. It was in 1852, during

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the early stages of his five years of field work on the upper Rio Negro in Amazonian Brazil, that Spruce first learned of caapi amongst the Tukanoan tribes of the region. It was employed to induce, for prophetic and divinatory purposes, an intoxication characterized, amongst other strange syndromes, by frighteningly realistic colored visual hallucinations and a feeling of extreme and reckless bravery. Unlike many early reports of newly discovered narcotics, Spruce's contribution included a precise determination of the botanical source of the drug.

Finding caapi cultivated along the Rio Negro, he noted that "there were about a dozen well growing plants . . . twining up to the tree tops . . . and several smaller ones. It was fortunately in flower and young fruit; and I saw, not without surprise, that it belonged to the . . . Malpighiaceae . . ." A collection in full flower (*Spruce 2712*) was taken from the liana, and he drew up a description of the species from living specimens. He allocated the species to the genus *Banisteria*, calling it *Banisteria Caapi* from the vernacular name. This description was published by the botanist Grisebach. As taxonomic understanding of the family grew in the present century, the American specialist, C. V. Morton, ascertained that this species-concept could not with precision be included in *Banisteria*, and, in 1931, he transferred it to the genus *Banisteriopsis*. The liana is, accordingly, now correctly called *Banisteriopsis Caapi* (*Spruce ex Grisebach*) Morton. *

Even a century ago, Spruce's thinking was, at least in part, along chemotaxonomical directions. He mused:

****Banisteriopsis Caapi*** (*Spr. ex Griseb.*) Morton in Journ. Wash. Acad. Sci. 21 (1931) 485.

Banisteria Caapi Spruce ex Grisebach in Martius Fl. Bras. 12, pt. 1 (1858) 43.

BANISTERIOPSIS *Caapi*
(*Spruce ex Griseb.*) Morton



1, flowering branch, about $\frac{1}{2}$ X. 2, flower, about $2\frac{1}{2}$ X. 3, fruit, somewhat larger than $\frac{1}{2}$ X.

“My surprise arose from the fact that there was no narcotic malpighia on record, nor indeed any species of that order with strong medicinal properties of any kind. *Byrsonima* . . . includes many species . . . their bark abounds in tannins . . . Another genus—*Bunchosia* . . . of the Andes . . . is described in books as poisonous, and if it be really so, then it is the only instance, so far as I know, of the existence of any hurtful principle in the entire family . . . excepting . . . caapi.” “Yet,” he prophetically remarked “strong poisons may lurk undiscovered in many others of the order, which is very large . . . ; and the closely allied soapworts (Sapindaceae) contain strong narcotic poisons, especially in the genus *Paullinia*.”

In many ways, Spruce was ahead of his times. In those years, there was little liaison between botanical explorers and chemists of the laboratory. Botanists seldom gathered material for phytochemical study, and in Spruce’s case the great distance and isolation of his scene of field work and the primitiveness and absence of normal communications one might believe would have made it impracticable or impossible for him to gather material in bulk for pharmaceutical specialists. Notwithstanding these drawbacks, Spruce did so enrich science, but, like so many collectors even in modern times, he was frustrated in his attempt.

“I obtained a good many pieces of stem [from the type plant of *Banisteria Caapi*], dried them carefully, and packed them in a large box, which contained the botanical [herbarium] specimens, and dispatched them down the river for England in March 1853. The man who took that box and four others on freight, in a large new boat he had built on the Uaupés, was seized for debt when about half-way down the Rio Negro, and his boat and all its contents confiscated. My boxes were thrown



RICHARD SPRUCE

Drawn by ELMER W. SMITH

aside in a hut, with only the damp earth for floor, and remained there many months, when my friend Senhor Henrique Antonij of Manáos . . . succeeded in redeeming them and getting them sent to the port of Pará. When Mr. Bentham came to open them in England, he found the contents somewhat injured by damp and mould, and the sheets of specimens near the bottom of the boxes quite ruined. The bundle of the caapi would presumably have quite lost its virtue from the same cause, and I do not know that it was ever analyzed chemically; but some portion of it should be in the Kew Museum at this day."

In an address at the III International Pharmacological Congress in São Paulo, Brazil, in 1966, one of the authors (2, 2a) said: "One of the most interesting exercises that I can imagine would be the analysis of a small portion of this original Spruce material—if, indeed, it is still preserved at Kew—with our modern improved chemical techniques. The active principles of caapi (harmine type alkaloids) might not have deteriorated with the mildew, and it is possible that even in this more than a century of storage, the alkaloids would be intact."

In later discussions of this interesting experiment, we resolved to try to follow it up. Accordingly, on December 21, 1967, we wrote to Sir George Taylor, Director of the Royal Botanic Gardens, Kew, and requested a small amount of the stem material of *Banisteriopsis Caapi* to which Spruce had referred, if it still existed. Shortly thereafter, Sir George and Dr. Patrick Brenan, Keeper, located this valuable historical collection and, on April 26, 1968, sent a letter informing us that some of this material would be made available for chemical study. Also enclosed were notes on the material from the entry book for 1854. The label on the specimens states:

"Stems of *Banisteria* sp. used with the roots and leaves

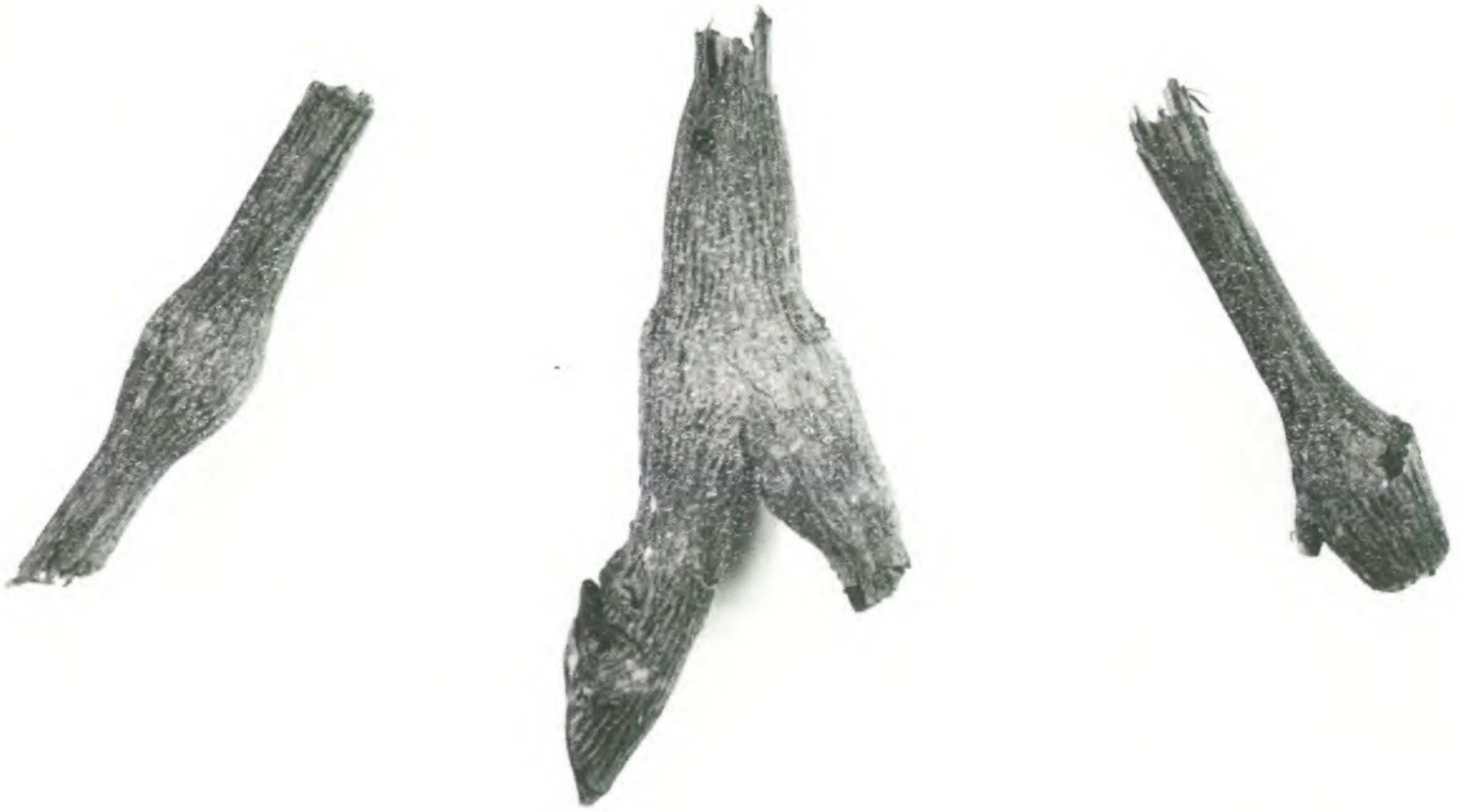
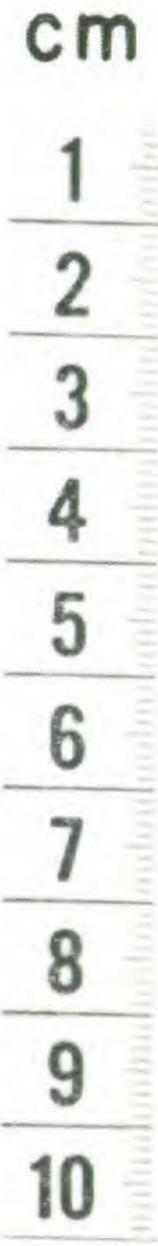
of *Haemadictyon* in the preparation of an intoxicating beverage called 'Caapi'. Rio Uaupes. *R. Spruce 166. HB 2712.*"

The entry in the notebook reads as follows:

"Portions of the stems of a Malpighiaceae twiner, apparently an undescribed *Banisteria* (2712 to Benth.), called by the Indians Caá-pi; and of the roots and leaves of a *Haemadictyon*, called *Caapí-pinima* (i.e. 'painted caapí') the leaves being veined with red. From these ingredients, the *Banisteria* entering much more largely than the *Haemadictyon*, is prepared an intoxicating drink known to all the natives on the Uaupés by the name of *Caapí*.

"In the Dabocurés (or festas) of the Uaupé Indians, the young men who figure in the dances drink of the Caapí 5 or 6 times during the night, the dose being a *cuya*, the size of a very small teacup, twice filled. In two minutes after drinking it, its effects begin to be apparent. The Indian turns deadly pale, trembles in every limb, and horror is in his aspect; suddenly contrary symptoms succeed—he bursts into a perspiration and seems popeyed with reckless fury—seizes whatever arms are at hand, his *murucú*, cutlass, or bow and arrows, and rushes to the doorway, where he inflicts deadly wounds on the ground or doorposts, calling out 'Thus would I do to such a one (naming some one against whom he has a grudge) were he within my reach.' In the space of 10 minutes, the effect passes off, and the Indian becomes calm, but appears much exhausted."

The parts of Spruce's material that reached the Department of Toxicology, Karolinska Institutet, Stockholm, in April 1968 consisted of five pieces weighing in all 26.7 g. (Plate XXXI); 11.5 g. were worked up for analysis by gas chromatography-mass spectrometry and other methods as described earlier (3, 4). The yield of



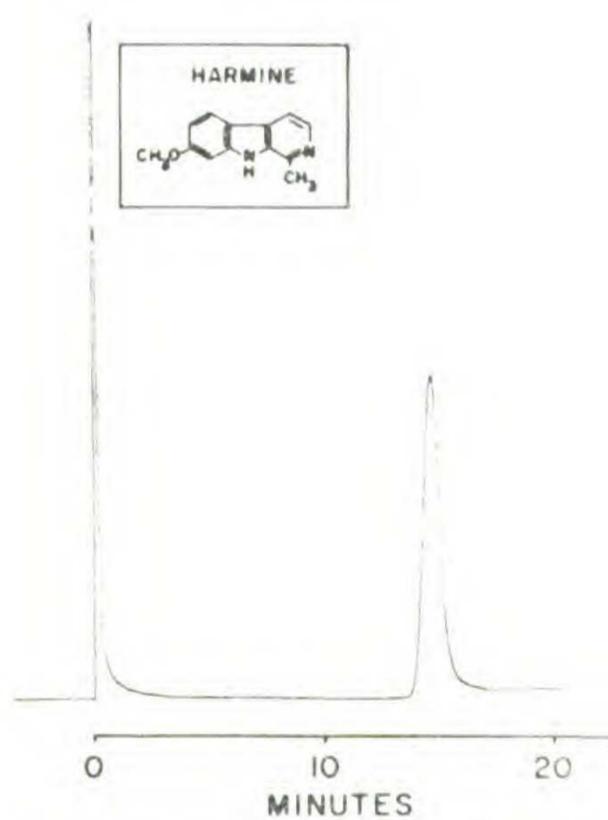
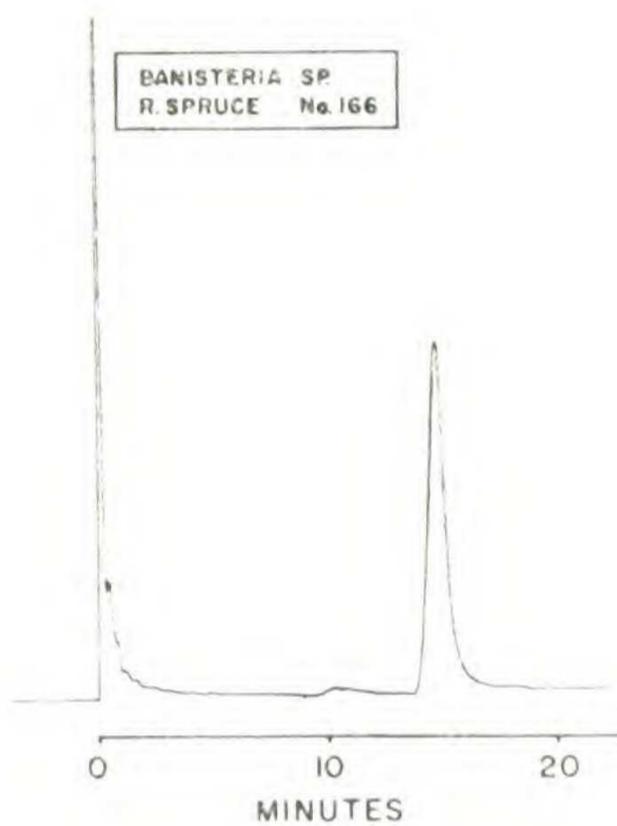
Banisteriopsis Caapi (Spr. ex Griseb.) Morton. R. Spruce No. 166.

alkaloids was found to be 0.4 per cent. A newly collected botanically verified specimen of *Banisteriopsis Caapi* analyzed at the same time was found to contain 0.5 per cent alkaloids (5). The latter material contained as described by many authors the main alkaloids harmine, harmaline and tetrahydroharmine (6). In addition, it contained two minor components that will be described separately (5). By contrast, the alkaloid content of the Spruce material *consisted exclusively of harmine*. This was proven beyond any doubt by gas chromatography and the combination of gas chromatography-mass spectrometry. As evident from both the gas chromatograms (Plate XXXII) and the mass spectra (Plate XXXIII), there is complete identity between synthetic harmine and the alkaloid in Spruce's material. It is open to question whether the stems sent home by Spruce in 1853 from the beginning contained only harmine or perhaps more likely that harmaline and tetrahydroharmine have with time been transformed into the chemically more stable aromatic β -carboline, harmine.

Under any circumstances, it is remarkable that Spruce's query about the chemical analysis of the material that fared so badly on its way from the Amazonian rain forest to the Royal Botanic Gardens at Kew has been answered by modern analytical microtechniques 115 years later.

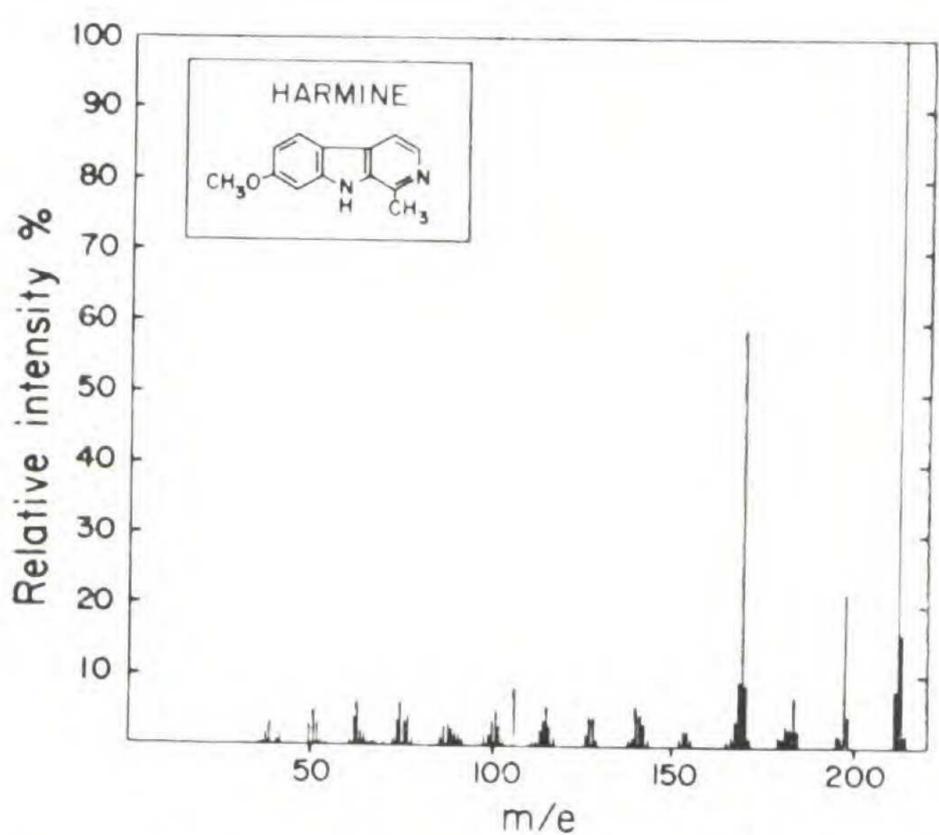
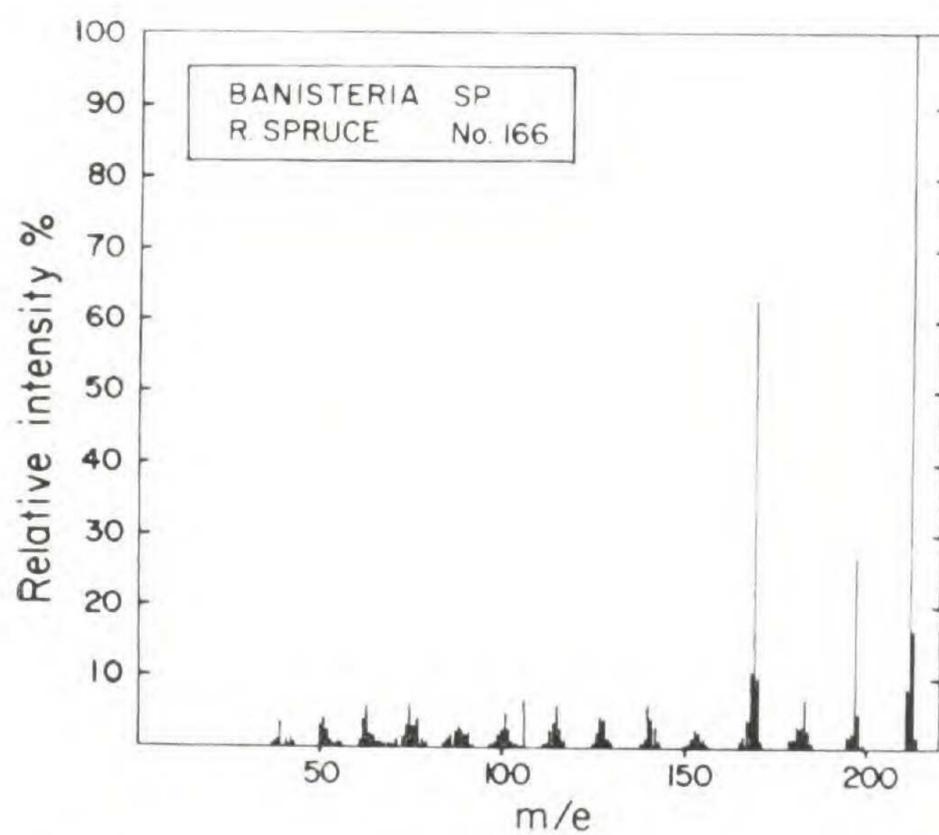
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PLATE XXXII



Gas chromatogram of alkaloid fraction from Spruce's material and reference substance. *Conditions:* Column 2 m ; i.d. 3.2 mm ; 5% OV-17 on 100-120 mesh Gas Chrom P ; temp. 230°.

PLATE XXXIII



Mass spectra of peaks shown in Plate XXXII. Conditions as described in Plate XXXII.

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